Sodium and chloride levels in rainfall, mist, streamwater and groundwater at the Plynlimon catchments, mid-Wales: inferences on hydrological and chemical controls

C. Neal, J. W. Kirchner

▶ **To cite this version:**

C. Neal, J. W. Kirchner. Sodium and chloride levels in rainfall, mist, streamwater and groundwater at the Plynlimon catchments, mid-Wales: inferences on hydrological and chemical controls. Hydrology and Earth System Sciences Discussions, 2000, 4 (2), pp.295-310. hal-00304610

HAL Id: hal-00304610
https://hal.science/hal-00304610

Submitted on 1 Jan 2000

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Hydrology and Earth System Sciences, 4(2), *295–310* (2000) © EGS

Hydrology & Earth System Sciences

Sodium and chloride levels in rainfall, mist, streamwater and groundwater at the Plynlimon catchments, mid-Wales: inferences on hydrological and chemical controls

Colin Neal[1] and James W. Kirchner[2]

[1]Centre for Ecology and Hydrology, Crowmarsh Gifford, Wallingford, Oxon OX10 8BB, UK.
[2]Department of Earth and Planetary Science, University of California, Berkeley, CA 94720-4767, USA.
e-mail for corresponding author: cn@ceh.ac.uk

Abstract

Variations in sodium and chloride in atmospheric inputs (rainfall and mist), stream runoff and groundwater stores are documented for the upper Severn River (Afon Hafren and Afon Hore catchments), Plynlimon, mid-Wales. The results show five salient features.

1. Sodium and chloride concentrations are highly variable and highly correlated in rainfall and mist. The sodium-chloride relationship in rainfall has a slope close to the sodium/chloride ratio in sea-water, and an intercept that is not significantly different from zero. This indicates that sea-salt is the dominant source of both sodium and chloride in rainfall, which would be expected given the maritime nature of the metrology. For mist, there is also a straight line with near-zero intercept, but with a slightly higher gradient than the sea-salt ratio, presumably due to small additional sodium inputs from other sources.
2. There is an approximate input-output balance for both sodium and chloride, with the exception of one groundwater well, in which high chemical weathering results in an anomalous high Na/Cl ratio. Thus, atmospheric deposition is the dominant source of both sodium and chloride in groundwater and streamflow.
3. The fluctuations in sodium and chloride concentrations in the streams and groundwaters are strongly damped compared to those in the rain and the mist, reflecting the storage and mixing of waters in the subsurface.
4. On all timescales, from weeks to years, sodium fluctuations are more strongly damped than chloride fluctuations in streamflow. The additional damping of sodium is consistent with ion exchange buffering of sodium in the catchment soils.
5. Sodium and chloride concentrations are linearly correlated in the streams and groundwaters, but the slope is almost universally less than the sea-salt ratio and there is a non-zero intercept. The Na/Cl ratio in streamflow and groundwater is higher than the sea-salt ratio when salinity is low and lower than the sea-salt ratio when salinity is high. This pattern of behaviour is again consistent with ion exchange buffering of sodium in the catchment soils.

The core features of this study are two fold. Firstly, sodium and chloride concentrations are highly damped within the streams and groundwaters relative to the atmospheric input. Secondly, streamflow sodium and chloride respond in similar ways across the catchments, except for the added cation exchange damping of the sodium signal. These findings are remarkable given the heterogeneous nature of the catchments and the complexity of the chemical time series signals in the streams.

Keywords: Sodium; chloride; rainfall; mist; stream water; groundwater; Plynlimon; Hafren; Hore; Tanllwyth; moorland; Sitka spruce; forest; cation exchange; fractal

Introduction

Over the past 20 years or more, great strides have been made in modelling the mechanisms that control water quality in catchments and river basins (Kämäri *et al.*, 1989). At the forefront of this research has been the production of dynamic and steady state models describing soil and surface water acidification (e.g. Cosby *et al.*, 1985a,b; Kirchner, 1992). Realistically integrating geochemical and hydrological processes remains a key challenge in catchment modelling. For example, consider the Birkenes model (Christophersen *et al.*, 1982, 1984), widely used in acidification research in the early 1980s (Mason, 1990). This model described temporal changes in stream acidity well, and simulated the determinands of direct concern (hydrogen ions, aluminium, alkalinity and sulphate). However, it proved impossible to fit these determinands of direct concern simultaneously with chemically unreactive species

such as chloride and the stable isotopes of hydrogen and oxygen (Neal *et al.*, 1988; Christophersen and Neal, 1990; Christophersen *et al.*, 1993). The lack of fit for unreactive species demonstrated that the model's hydrologic premises were inadequate, even though reactive species could be simulated successfully. This feature indicated either that the unrealistic aspects of the hydrological model were inconsequential, or that they could be masked by parameter tuning in the geochemical equations (Hooper *et al.*, 1988; Kirchner *et al.*, 1996). Recently, a new modelling study using chloride as an unreactive tracer at the Plynlimon catchments in mid-Wales, indicates that the rainfall signal is attenuated from a "white noise" input signal into a fractal output (Kirchner *et al.*, 2000). This work adds to the growing evidence for the Plynlimon catchments, and elsewhere, of highly complex flow routing within catchments that have previously been modelled as relatively simple systems (Neal, 1997b; Neal *et al.*, 1997b,c,d).

This paper presents the first description of the full sodium and chloride data record at Plynlimon for atmospheric inputs (rainfall and mist), groundwater, and stream outputs across a range of scales, and documents the extent of catchment damping of the atmospheric inputs. Sodium takes part in adsorption-desorption reactions involving cation exchange processes in the soil (Garrels and Christ, 1965), whereas the Plynlimon soils should have little sorption capacity for chloride. Further, unlike the other relatively abundant base cations (K, Mg, Ca) which also take part in such exchange processes, sodium is the only one that comes primarily from the atmosphere and has few weathering sources within the Plynlimon catchments (Neal *et al.*, 1997e).

By exploring the relationships between sodium and chloride, the main atmospheric inputs to the Plynlimon catchments, this work provides an important test of the efficacy and nature of cation exchange processes in catchments. Such tests are needed because the applicability of cation exchange models has been questioned (Neal, 1997b). If cation exchange reactions are important for sodium, then the relationship between sodium and chloride in rainfall should be altered in the soil solution by ion exchange buffering. When sodium concentrations are high, more sodium should be adsorbed onto cation exchange sites in the soils, thus lowering the Na/Cl ratio below what it otherwise would have been. Conversely, when sodium concentrations are low, sodium should be desorbed from cation exchange sites, thus raising the Na/Cl ratio. This buffering of the Na/Cl ratio should also be evident in the stream waters, which arise through drainage of the soil solution.

The cation exchange process cannot be observed easily in the other cation exchange components (the base cations as well as hydrogen ions and inorganic aluminium), because these are usually dominated by chemical gradients within the catchments. These gradients are associated with the contrast between the acidic soils and the more alkaline underlying bedrock, which is the dominant source of weathering products. Because hydrological fluctuations at Plynlimon alter the relative contribution of near-surface soil porewater and deeper bedrock fracture flow, they vary the concentrations of these other cations over time (Neal and Christophersen, 1989; Neal *et al.*, 1990a,b). Thus, hydrological fluctuations can largely mask the cation exchange process for these other cations.

This paper addresses three main questions with the Plynlimon data.

1. To what extent is the atmospheric input of sodium and chloride damped within the catchments?
2. How uniform is the damping across the catchments?
3. Do cation exchange processes regulate sodium mobility within the catchments—as seen within the stream and the groundwater?

These questions are of fundamental importance within catchment research, as

- Cation exchange mechanisms potentially provide a major moderating influence on the impacts of acidic deposition (e.g. Christophersen *et al.*, 1982, 1984; Cosby *et al.*, 1985a,b; Kirchner, 1992);
- Fractal scaling in stream chemistry at Plynlimon indicates a power-law travel time distribution for waters flowing through the catchments, and thus implies slower recovery rates from contaminant inputs than would be predicted by widely used environmental impact models (Kirchner *et al.*, 2000);
- The Plynlimon case does not seem to be atypical (Neal, 1997b; Kirchner *et al.*, 2000).

Study area

The data described in this report come from wide ranging studies at the Centre for Ecology and Hydrology catchment research sites at Plynlimon in mid-Wales. The hydrology, biology and water quality of these sites, and the Plynlimon research have been described in a Special Issue of Hydrology and Earth Systems Sciences (Neal, 1997a), where extensive background information can be obtained. Figure 1 provides a location map with the monitoring sites specific to the present paper, and the analytical methodologies with sampling protocols etc. are provided by Neal *et al.* (1992, 1997e). Background information, including soil and vegetation types and lengths of record is provided in Table 1. For this Table, the headings have had to be abbreviated and the key to the tables is as follows:

- **Site**, UHa = Upper Hafren, LHa = Lower Hafren, UHo = Upper Hore, LHo = Lower Hore, Tan = Tanllwyth, S2Ho = South-2 Hore, SE1 = South East-1, SE3 = South East-3, TanN = Tanllwyth North, TanS = Tanllwyth South. Note that the HA4 and LS4 boreholes represent the same site: "LS" data correspond to a monthly sampling for one year only

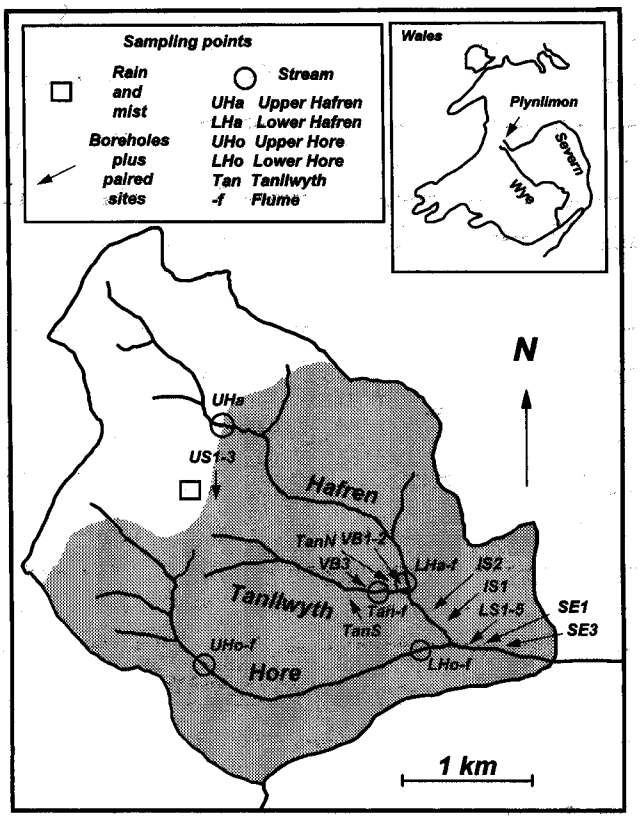

Fig. 1. *The Plynlimon study area.*

while the HA4 borehole data include weekly sampling after the first year of sampling. For the paired sites with control and felled catchments, the suffix "c" represent control sites while the suffix "f" represents felled sites.

- **The catchment area (Area)** is given in hectares.
- **Vegetation (Veg)** SS = Sitka Spruce; M = Acid Moorland.
- **Soil type (Soil)** G = Gley; P = Podzol; Pe = Peat, Gr = Gravel.
- **Occurrence of felling (Fell)** Y = Yes, 100% fell unless indicated otherwise; N = No, 0% fell. The superscripted felling dates in the fell column are 1, LHa, ongoing thinning; 2, LHo, March 1985 to October 1988; 3, Tan, February 1996; 4, S2Ho, August-October 1989; 5, SE1, September-October 1995; 6, TanN, February 1996.
- **Sampling rate (Samp)** is given as samplings per year.
- **The period of record** from the *Start* to the *End* date is also provided (Cont = continuing, but for the present analysis, the data cover up to the end of December 1998). The italics for Rain, LHa and Tan represent the detailed daily sampling record for chloride (see item 4 below).

A brief summary of the information for each area follows. Four types of monitoring sites are present at Plynlimon.

1. There are long term monitoring sites for the main tributaries of the headwaters of the River Severn. These drain a hill top plateau region dominated by acid moorland in the upper portion of the catchment and the Hafren Forest. Catchment areas for these sites vary from about 50 to 300 ha. The moorland and forest catchments represent a mixture of upland acid soil types dominated by peaty podzols with subsidiary peaty gleys; deep peats are also important in the moorland plateau area. In total, five streams are monitored regularly, one moorland (upper Hafren: UHa) and four mainly forested streams: lower Hafren (LHa), which includes the moorland drainage from the upper Hafren; the entirely forested Tanllwyth (Tan); the upper Hore (UHo), and the lower Hore (LHo). The forest area in the lower Hore catchment was clearfelled during the mid- to late- 1980s. For the other sites, some localised felling has taken place over many years to thin and in some cases harvest small areas of the crop, and about half of the Tanllwyth catchment was felled in February 1996. Hafren Forest comprises mainly Sitka spruce (*Picea sitchensis*) with some Norway spruce (*Picea abies*), larch (*Larix* spp) and lodgepole pine (*Pinus contorta*) planted in various phases from the mid-1940s through to the late-1960s. A variety of harvesting techniques has been used, but in most areas only the tree stem has been removed from site leaving the felling debris (stumps, branches and needles) behind. Across the area, the bedrock comprises fractured Lower Palaeozoic mudstones, shales and grits.
2. There has been a series of eight small catchment studies (<15 ha) examining explicitly the interaction between soil type and forest harvesting on water quality. In most cases a paired catchment approach has been applied with control and wholly manipulated forested catchments. Six of these sites are located within Hafren Forest at Plynlimon and represent two of the main soil types of concern, peaty podzols (S2Ho, SE1, SE2, SE3) and peaty gleys (Tan-N, Tan-S). The manipulated sites at Plynlimon are S2Ho, SE2, SE3 and Tan-N. The site names for the paired catchments are given in the text and tables with the suffix "f" for felling and "c" for control.
3. Thirteen exploratory and six monitoring boreholes were drilled to monitor groundwater chemistry and water levels within the Hafren catchment. The exploratory boreholes were established in 1984 throughout the catchment to examine upper plateau (UP1,2,3), intermediate slopes (IS1,2), lower slopes (LS1,2,3,4) and the valley bottom (VB1) to cover a full range of geomorphological environments. These exploratory boreholes were monitored for one year on a monthly basis and one site (LS4) was subsequently monitored weekly (listed within the tables as Hafren site HA4). The six monitoring boreholes were established in 1995 near the paired catchments to provide an assessment of groundwater quality changes at felling and control sites. They

Table 1. Catchment summary information.

Site	Area	Soil	Veg	Fell	Samp	Start	End
				Atmospheric inputs			
Rain	–	–	–	–	52	10/5/83	Cont
Rain	–	–	–	–	*365*	*20/4/94*	*13/6/97*
Mist	–	–	–	–	52		Cont
				Main streams			
Uha	117	M/Pe	M	M	52	17/7/90	Cont
LHa	347	M/P/G	SS	Y < 25%[1]	52	10/5/83	Cont
LHa	*347*	*M/P/G*	*SS*	*Y < 25%[1]*	*365*	*20/4/94*	*13/6/97*
Uho	178	M/P/G	SS	N	52	28/8/84	Cont
Lho	335	M/P/G	SS	Y50%[2]	52	10/5/83	Cont
				Intermediate size stream			
Tan	51	G	SS	Y50%[3]	52	17/9/91	Cont
Tan	*51*	*G*	*SS*	*100*	*365*	*20/4/94*	*13/6/97*
				Small streams			
S2Ho	3–6	P	SS	Y100%[4]	52	19/4/88	Cont
SE1f	2–4	P	SS	Y100%[5]	26	20/9/94	Cont
SE3c	2–4	P	SS	N	26	11/10/94	Cont
TanN	<2	G	SS	N[6]	26	28/4/94	Cont
TanS	<2	G	SS	Y100%	26	28/4/94	Cont
				Boreholes			
HA4b		P	SS	Y100%[5]	12/52	24/04/94	Cont
SE1bf		P	SS	Y100%[5]	26	10/05/95	Cont
SE3bc		P	SS	N	26	10/05/95	Cont
TanNbc		G	SS	N[6]	26	05/07/94	Cont
TanSbf		G	SS	Y100%	26	09/08/94	Cont
US1		Pe	M	M	12	24/04/94	12/07/95
US2		P	SS	N	12	24/04/94	12/07/95
US3		P	SS	N	12	24/04/94	14/06/95
US4		P	SS	N	12	24/04/94	12/07/95
LS1		P	SS	N	12	24/04/94	12/07/95
LS2		P	SS	N	12	17/05/94	12/07/95
LS3		P	SS	N	12	24/04/94	12/07/95
LS4		P	SS	N	12	24/04/94	12/07/95
IS1		P	SS	N	12	24/04/94	12/07/95
IS2		P	SS	N	12	24/04/94	12/07/95
VB1		P/Gr	M	M	12	24/04/94	12/07/95

are described by the same scheme as the paired catchments although the suffix "b" is used to denote that they are borehole sites.

4. Weekly information, while characterising the broad patterns of water quality and flow change cannot be relied upon to capture the details of dynamic water quality and hydrological change. For example, rainfall events and hydrograph responses often spanned less than a week (typically a day or two): an earlier simulation by Robson (1993) on sampling frequency required to characterise flow (based on 15 minute interval data) indicated that daily sampling was more appropriate. Consequently, to see if the damping of the rainfall chloride observed in the stream was an artefact of the sampling frequency and to examine the dynamics of the rainfall-runoff relationships for chloride, daily

rainfall and stream water chloride concentrations and associated flows were measured. Two stream sites were chosen. One of these sites represents the main catchment with more permeable podzolic soils (lower Hafren), such that damping of the rainfall chloride signal in the stream might be expected. The other site (Tanllwyth) represents soils of low permeability (gleys), with a much higher potential for near-surface runoff and lower water storage; it is here where the rainfall signal might best be discernible in the stream. These stream sites and rainfall (at a nearby meteorological site) were monitored daily between April 1994 and June 1997.

Results

RATIONALE

The results of the work are presented within Tables 2–4. Here, summary statistics are provided for chloride, sodium and the ratio of sodium to chloride, respectively, for the rainfall, the main streams (the main channels of the Hafren and Hore), the intermediate sized stream (the Tanllwyth), the small streams and the borehole sites. Within the tables, the ratio of the standard deviation to the mean is provided as an assessment of the scatter in the data, in order to allow for differences between the mean values for the different sites. Further, within the tables, standard and flow-weighted means are presented for the rainfall, mist and streams to allow consideration of variation of both concentration and flux. For the smaller streams, which have not been gauged, flow data for the nearest main stream gauge have been used for the flow-weighting. For the boreholes, flow-weighted values could not be calculated, because only water level was recorded. In the case of the sodium to chloride ratio, the means are calculated as straight averages of the ratio, the ratio of the average-sodium to average-chloride and the ratio of the average-flow-weighted-sodium to average-flow-weighted-chloride to cover different aspects of the analysis. For example, in the case of the rainfall and mist samples, very low sodium values below the analytical detection level and correspondingly low chloride values are sometimes observed. It is not appropriate to calculate a representative ratio in this case: a sodium to chloride ratio of zero would result in an underestimate of the mean. The flow-weighted means and the ratio of the average-flow-weighted-sodium to average-flow-weighted-chloride is used to consider mass balance transfers of sodium and chloride from rainfall to the stream: the straight means are only used for statistical summaries.

To summarise the large amount of information presented and to simplify the analysis, three different aspects are considered separately below: mean values, ranges and sodium-chloride inter-relationships.

GENERAL RELATIONSHIPS IN MEAN SODIUM AND CHLORIDE CONCENTRATIONS

Sodium and chloride in the rainfall, mist, stream water and groundwaters have concentrations whose averages vary in the range 114 to 1508 and 89 to 1366 μ Eq l^{-1}, respectively. The variations in mean concentrations exhibit systematic differences for the differing water types and there are eight main aspects to this.

1. The highest mean and flow-weighted mean concentrations for sodium and chloride occur for mist. Concentrations in mist are an order of magnitude higher than in the rainfall. This is a characteristic feature of the area. Indeed, mists are generally enriched in sea salts relative to rainfall for maritime areas due to the presence of sea-salt aerosols and their partial to complete evaporation within the atmosphere (Cryer, 1986).
2. The mean sodium and chloride concentrations are highly correlated for all the water types monitored. Thus, linear regression indicates a strong linear feature with an intercept insignificantly different from zero:

$$[\text{Average Na}] = 0.896 \pm 0.044^{*}$$

$$[\text{Average Cl}] + 16.44 \pm 28.2$$

   where $r^2 = 0.949$ and $N = 27$: the $\pm$ sign indicates plus or minus twice the standard error. This gradient is close to that for sea-water (0.857: Drever, 1997) illustrating the net effect of the maritime nature of the sodium and chloride input and the lack of significant weathering sources in the catchment: deviations from this line occur for the individual sites as discussed below.
3. In terms of the importance of mist contributions to atmospheric deposition, earlier work showed that the annual rainfall (2518 mm) is augmented by a mist component, which accounts for a volumetric input of 33 and 140 mm for moorland and forest, respectively, for the Plynlimon area (Wilkinson *et al.*, 1998). This means that the contribution of mist to the atmospheric deposition input of sodium and chloride is about 11% for the moorland areas and about 33% for the forested areas (Table 5).
4. The rainfall concentrations for both sodium and chloride are lower than in the streams and groundwaters by a factor ranging from about 40% to about three-fold. This difference reflects both the increased scavenging of mist by the vegetation and the evaporation (interception loss plus transpiration) of water from the catchments.
5. Within the main streams, there is a general variation in mean concentration, for both sodium and chloride, in the sequence LHa < S2Ho < LHa $\approx$ UHo $\approx$ LHo < Tan. This feature represents an ordered sequence of forestry cover (after allowing for partial felling of the catchments part way through the sampling period).

Table 2. The variation of chloride in rainfall, mist, stream water and groundwater at Plynlimon. All concentration units are μ Eq l^{-1}.

	avg.	fw-avg.	min	max	std	std/avg
Atmospheric inputs						
Rain	115	126	6	1241	131.2	1.14
Mist	1508	1269	48	20875	1815.5	1.20
Main streams						
Uha	162	163	99	381	24.3	0.15
LHa	200	202	110	482	35.0	0.17
Uho	206	214	107	564	44.4	0.22
Lho	212	208	107	615	43.1	0.20
Intermediate size stream						
Tan	228	246	116	564	44.9	0.20
Small streams						
S2Hore	205	198	82	719	90.6	0.44
SE1f	261	252	158	361	48.0	0.18
SE3c	211	209	135	440	37.8	0.18
TanNc	224	303	99	987	111.9	0.50
TanSf	197	219	48	564	80.1	0.41
Boreholes						
Ha4b	305		260	355	22.5	0.07
SE1bf	254		141	310	25.1	0.10
SE3bc	308		240	480	49.3	0.16
TanNbc	265		104	327	43.8	0.17
TanSbf	284		183	361	29.5	0.10
US1	229		152	333	57.3	0.25
US2	288		237	316	21.3	0.07
US3	200		161	231	24.1	0.12
LS1	300		271	338	17.4	0.06
LS2	324		299	350	15.8	0.05
LS3	322		293	355	19.2	0.06
LS4	326		279	378	24.9	0.08
IS1	305		243	367	30.6	0.10
IS2	338		310	395	22.2	0.07
VB1	149		130	172	13.0	0.09
Daily samples						
Rain	125	94	0	1495	166.7	1.34
LHa	188	184	110	271	17.0	0.09
Tan	217	211	102	372	23.5	0.11

Indeed, using flow-weighted values, which provide the best measure for flux transfers, good linear relationships occur for both sodium and chloride concentrations when correlated against the percentage of forest cover. Thus,

$$Na(\mu Eq\,l^{-1}) = 0.592 \pm 0.214^{*}\%forest + 151.1 \pm 14.9 \quad (r^2 = 0.884)$$

and

$$Cl(\mu Eq\,l^{-1}) = 0.782 \pm 0.351^{*}\%forest + 175.5 \pm 24.4 \quad (r^2 = 0.883)$$

where the $\pm$ sign indicates plus or minus twice the standard error and N = 6 in both cases. These equations provide estimates for the moorland and the forest of 151

Table 3. The variation of sodium in rainfall, mist, stream water and groundwater at Plynlimon. All concentration units are μ Eq l^{-1}.

	avg	fw-avg	min	max	std	std/avg
Atmospheric inputs						
Rain	89	102	0	1026	105.5	1.19
Mist	1366	1134	55	18226	1567.7	1.15
Main streams						
Uha	152	147	81	265	13.4	0.09
LHa	177	172	99	302	18.8	0.11
Uho	176	176	63	396	24.7	0.14
Lho	183	174	92	379	21.0	0.11
Intermediate size stream						
Tan	213	207	140	327	25.6	0.12
Small streams						
S2Ho	177	164	90	720	56.3	0.32
SE1f	272	258	182	325	27.8	0.10
SE3c	205	201	146	299	18.2	0.09
TanNc	204	233	133	540	55.2	0.27
TanSf	182	172	84	388	55.8	0.31
Boreholes						
Ha4b	323		279	386	24.2	0.08
SE1bf	259		230	322	16.4	0.06
SE3bc	284		240	361	20.2	0.07
TanNbc	231		141	346	44.0	0.19
TanSbf	259		229	395	21.4	0.08
US1	245		200	313	35.5	0.15
US2	265		239	278	10.7	0.04
US3	176		152	209	17.6	0.10
LS1	292		265	317	13.8	0.05
LS2	311		261	330	15.3	0.05
LS3	304		265	322	15.7	0.05
LS4	340		306	387	25.7	0.08
IS1	289		248	344	21.5	0.07
IS2	314		274	361	17.1	0.05
VB1	259		139	591	168.6	0.65

and 210 μ Eq l^{-1} for sodium and 175 and 254 μ Eq l^{-1}, respectively, for chloride.

6. The relationships between forested and moorland catchments described in (4) and (5) are not as clearly represented for the smaller, higher-alkalinity catchments for either sodium or chloride. This is to be expected because the smaller, higher-alkalinity catchments show much more heterogeneous behaviour in their chemistries and the relative importance of groundwater inputs and storage is much higher (Neal *et al.*, 1997b,c,d; Neal *et al.*, 1998a,b).
7. The information used in sections three and four can be used to estimate the net evaporation for moorland and forest using the sodium and chloride data for the Upper Hafren (100% moorland) and the Tanllwyth (100% forest - only the period prior to felling is analysed). To do so, it is assumed that there is a net flux balance between the atmospheric input and the stream output for both sodium and chloride. By simple mass balance relationships, $P/Q = \{Na_{stream}\}/\{Na_{atmospheric\ input}\} = \{Cl_{stream}\}/\{Cl_{atmospheric\ input}\}$. For this equation, the {} terms represent flow weighted mean concentrations, P is the volumetric precipitation of water and Q is the volumetric flow (both in mm/annum units). The results show that P/Q is about 1.21 for the moorland and about 1.32 for the forest. These values compare reasonably

Table 4. The sodium to chloride ratio for rainfall, mist, stream waters and groundwaters at Plynlimon. The ratios represent the concentration ratios expressed in μ Eq l^{-1} units: avg-R, avg-MR and avg-FWR represents the average for average ratio, avg-Na/avg-Cl and (avg flow weighted Na)/(avg flow weighted Cl).

	avg-R	avgM-R	avgFW-R	min	max	std	std/avg
			Atmospheric inputs				
Rain	0.76	0.77	0.81	0.00	2.65	0.22	0.28
Mist	0.96	0.91	0.89	0.04	2.95	0.25	0.25
			Main streams				
UHa	0.95	0.94	0.90	0.47	1.14	0.09	0.10
Ha	0.90	0.88	0.85	0.52	1.54	0.10	0.11
UHo	0.86	0.85	0.82	0.58	1.24	0.09	0.11
Ho	0.88	0.86	0.84	0.40	1.52	0.10	0.12
			Intermediate size stream				
Tan	0.95	0.93	0.84	0.50	1.31	0.13	0.14
			Small streams				
S2Ho	0.91	0.87	0.83	0.51	1.28	0.14	0.15
SE1f	1.06	1.04	1.02	0.82	1.83	0.15	0.14
SE3c	0.98	0.97	0.96	0.51	1.14	0.09	0.09
TanNc	0.99	0.91	0.77	0.55	1.70	0.24	0.24
TanSf	0.99	0.92	0.78	0.48	2.23	0.28	0.28
			Boreholes				
Ha4bore	1.06	1.06		0.91	1.27	0.08	0.07
SE1bf	1.03	1.02		0.83	1.88	0.12	0.12
SE3bc	0.94	0.92		0.59	1.35	0.11	0.12
TanNbc	0.89	0.87		0.62	1.41	0.17	0.19
TanSbf	0.92	0.91		0.76	2.16	0.15	0.16
US1	1.11	1.07		0.85	1.36	0.21	0.18
US2	0.92	0.92		0.87	1.05	0.05	0.05
US3	0.88	0.88		0.81	0.97	0.04	0.04
LS1	0.98	0.97		0.88	1.11	0.07	0.07
LS2	0.96	0.96		0.83	1.03	0.05	0.05
LS3	0.95	0.94		0.87	1.05	0.05	0.05
LS4	1.05	1.04		0.87	1.27	0.10	0.10
IS1	0.95	0.95		0.87	1.04	0.05	0.05
IS2	0.93	0.93		0.85	1.03	0.05	0.05
VB1	1.68	1.74		0.97	3.74	1.00	0.59

well with hydrological estimates of 1.25 for the moorland and 1.33 for the forest based on the data for the adjacent River Wye and Severn catchments (Table 5). The results are particularly good for the forested systems where concentration differences between the atmospheric inputs and stream outputs are greatest and are most easily discerned.

8. Taking into account all the chemical estimates of evaporation based on the sodium and chloride information, as presented in Table 5, including moorland and forested endmember compositions determined in section five, above, the results show an average evaporation of 19.7% (496 mm) for the moorland and 24.9% (627 mm) for the forest. These averages are very close to those for the hydrological estimates (19.9% and 24.6%, respectively).
9. The results of the chemical and hydrological estimates of evaporation for the forested Tanllwyth differ significantly: the chemical results imply an evaporation loss of 680 mm while the hydrological estimate is about 200 mm (Hudson *et al.*, 1997) for the same period of record. Nonetheless, the results are similar when the

Table 5. An assessment of moorland and forest evaporation based on chemical and hydrological measurements as denoted by the ratio P/Q of precipitation (P in mm) to stream flow (Q-mm). The chemical estimates of P/Q are based on the sodium and chloride data for the Upper Hafren and the Tanllwyth, respectively. In the case of the Tanllwyth, the data refer to the period up to felling: the latter period was excluded as the data could not then be used to determine the forest endmember. For comparative purposes, the chemical estimates of P/Q have also been calculated based on moorland and forest endmembers calculated from the statistically based linear equations for sodium and chloride concentration versus percentage forestry cover described earlier in this paper. "P/Q chemistry" refers to the chemical estimates from this study and "P/Q hydrology" refers to the hydrological estimates of Hudson *et al.* (1997) for the period 1971–1995. For the calculation, the chemical values refer to flow-weighted mean estimates and the "Total input" refers to the mist and rainfall components. To assess the total input of sodium and chloride, figures of 33 and 140 mm of mist have been used to determine the volumetric mist component: these figures correspond to the values presented by Wilkinson *et al.* (1998) for the Plynlimon area. For the chemical estimates, comparative values have been estimated using moorland and forest endmember concentrations based on the regressions of concentration against % forest cover: the results are presented within brackets in the table. The % evaporation loss equals 100*(P – Q)/P.

		Na moorland	Na forest	Cl moorland	Cl forest
Rainfall	μ Eq l^{-1}	101.6	101.6	125.8	125.8
Mist	μ Eq l^{-1}	1134.2	1134.2	1268.9	1268.9
Total input	μ Eq l^{-1}	115.0	156.0	140.6	186.0
Solute input in mist	%	11.6	34.9	10.5	32.3
Stream	μ Eq l^{-1}	146.5 (151.1)	208.0 (210.3)	162.9 (175.4)	242.6 (253.6)
P/Q chemistry		1.273 (1.314)	1.333 (1.348)	1.159 (1.248)	1.304 (1.363)
P/Q hydrology		1.248	1.327	1.248	1.327
% evaporation loss chemistry	%	21.4 (23.9)	25.0 (24.6)	13.7 (19.9)	23.3 (26.6)
% evaporation loss hydrology	%	19.9	24.6	19.9	24.6

chemical estimates are compared with hydrological estimates for Severn catchments as discussed in 7 and 8. Within the hydrological study, there have been question marks over the use of above canopy gauges for measuring rainfall in the forested areas with an evolving (growing) canopy structure (Hudson *et al.*, 1997). The present study confirms the reservation: the hydrological balance estimate for the Tanllwyth system makes the most use of data from the above canopy gauges, and exhibits the greatest discrepancy with the chemical estimate of evaporation.

GENERAL VARIATIONS IN SODIUM AND CHLORIDE CONCENTRATIONS

The atmospheric inputs show a much greater variation in both sodium and chloride concentrations, compared to the streams and the groundwaters. This is illustrated within Tables 2 and 3 by the larger range, larger standard deviation and larger ratio of the standard deviation normalised to the mean for the rainfall and the mist compared to the streams and boreholes. For example, the maximum, standard deviation and standard deviation normalised to the mean are about five to ten times higher in rainfall compared to the stream and groundwater for both sodium and chloride; the differences for mist are even higher. This feature is observed for both the weekly and daily time series and there is little to discern between the patterns other than a lower flow-weighted mean for the daily samples, which cover a shorter time-span when presumably the incoming flux of sea salts is lower. The chloride results show the classic pattern reported for the Plynlimon catchments, where the stream water exhibits strongly damped response to fluctuations in rainfall chloride concentrations. Note however, that for the daily chloride time series for the Tanllwyth that the flow weighted average rainfall differs from the straight average.

Table 3 shows that sodium, like chloride, is strongly damped in streamflow and groundwater compared to rainfall and mist. The strong damping in streamflow is illustrated in Fig. 2, which shows individual weekly samples, 90-day moving averages, and annual moving averages, for sodium and chloride in rainfall and lower Hafren streamflow. The range of rainfall concentrations is visibly much larger than the range of streamflow concentrations. Note also that, whereas the seasonal fluctuations in runoff concentrations are uniformly small, the amplitudes of the rainfall concentration fluctuations vary greatly from year to year. The high rainfall chloride concentrations in 1990 boost streamflow chloride concentrations (grey solid line, Fig. 2c-d) for several years, illustrating the catchment's long-term "memory" for atmospheric inputs.

The strong damping in groundwater and streamflow

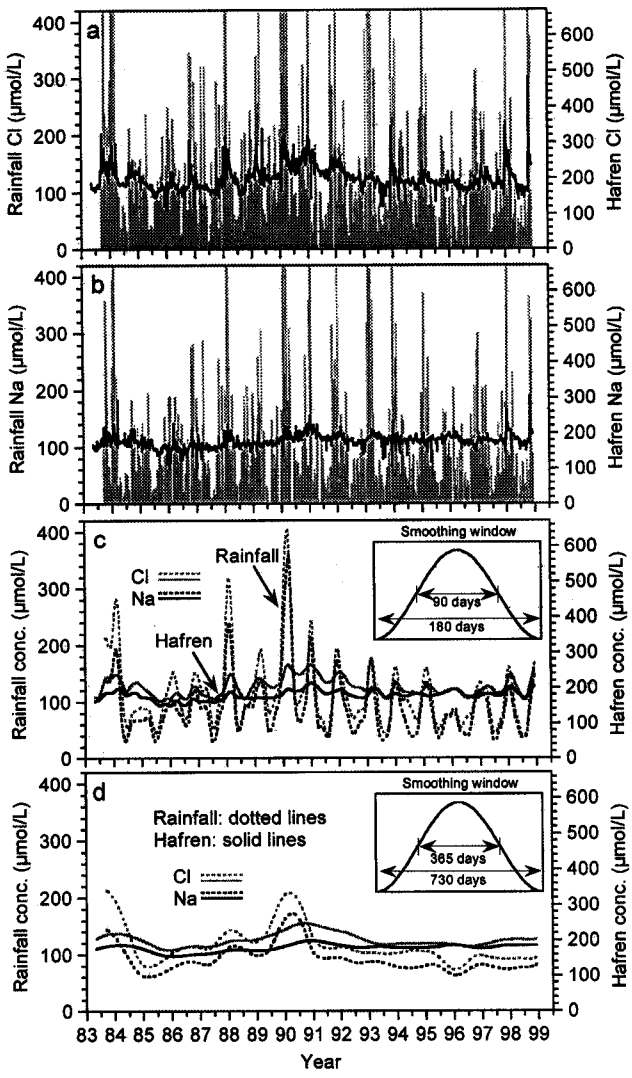

Fig. 2. *Fifteen years of weekly measurements of sodium and chloride concentrations in rainfall and lower Hafren streamflow at Plynlimon, mid-Wales. Panels (a) and (b) show that concentrations in streamflow (black lines) are damped significantly compared to rainfall (grey lines). Panels (c) and (d) show ninety-day and annual moving averages of sodium (black) and chloride (grey) in rainfall (dotted lines) and streamflow (solid lines). Seasonal fluctuations in rainfall concentrations (dotted lines, panel c) vary greatly from year to year; seasonal fluctuations in streamflow concentrations (solid lines) are much smaller. The streamflow concentration scale has been expanded by a factor of 1.60, to account for dry deposition and evapoconcentration; that is, the weighted average concentrations of chloride in rainfall and streamflow would overlap exactly on the graphs. The sinusoidal smoothing windows (see insets) have a total width that is twice their nominal size (90 and 365 days in panels (c) and (d) respectively), which is their width at half maximum.*

chloride concentrations indicates either that the groundwater store is large, or that the groundwaters are supplied from a large store within the catchment that has already damped the rainfall signal. In the streams and groundwaters, there is no statistically significant correlation of sodium and chloride concentrations with stream-flow/groundwater-level or the logarithm of stream-flow/groundwater-level. This confirms the lack of a significant weathering source for sodium and chloride. If weathering processes were important, the highest concentrations would be observed under baseflow conditions in the stream and groundwater levels would be low when supplies are dominated by longer residence time groundwater/bedrock sources.

Sodium concentrations are less variable than chloride concentrations (as expressed by the ratio of the standard deviation to the mean) in all ten of the streams, and in 12 of the 15 borehole monitoring sites (Tables 2 and 3). In rainfall and mist, by contrast, the variability of sodium is similar to that of chloride. Thus, both sodium and chloride fluctuations are strongly damped in streamflow and groundwater, but sodium is more strongly damped than chloride. The stronger damping of sodium is clearly visible in the lower Hafren time series (Fig. 3); on all timescales, from weeks to several years, the sodium fluctuations are visibly smaller than the chloride fluctuations.

Sodium and chloride time series in undisturbed catchments

Similar sodium and chloride time series are observed across all the catchments, with some minor differences due to

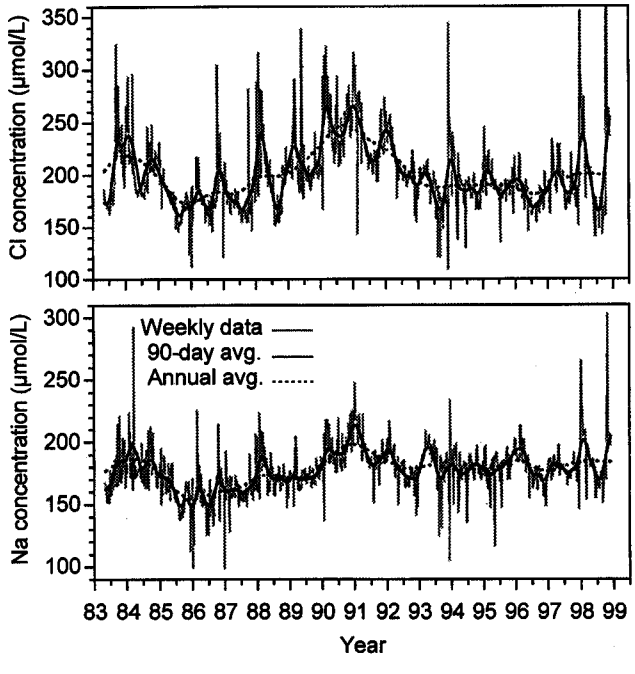

Fig. 3. *Concentrations of chloride (top panel) and sodium (bottom panel) in lower Hafren streamflow. Weekly measurements are shown in grey and 90-day and annual moving averages are shown by black solid and dotted lines, respectively. Sodium concentrations are less variable than chloride, on all timescales. The chloride concentration scale has been compressed by the sea-salt sodium/chloride ratio (0.86) to make the two scales comparable.*

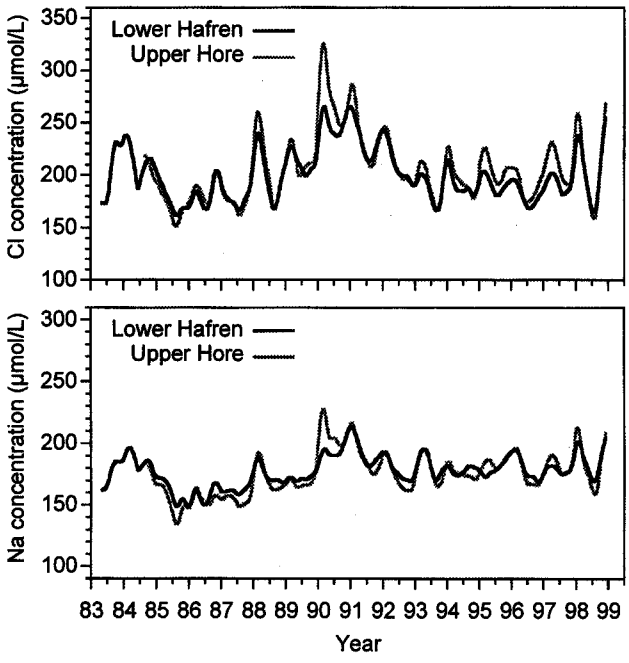

Fig. 4. *Ninety-day moving averages of chloride (top panel) and sodium (bottom panel) in streamflow at lower Hafren (black lines) and upper Hore (grey lines). The chloride concentration scale has been compressed by the sea-salt sodium/chloride ratio (0.86) in order to make the two scales comparable.*

felling. The similarities in the undisturbed catchments are illustrated in Fig. 4, which shows sodium and chloride data for two adjacent streams, the Lower Hafren and the Upper Hore, with similar forest cover (about 50%) and similar soils (podzols). Figures 3 and 4 show that:

1. the sodium and chloride track each other but with a higher damping for sodium;
2. the lowest sodium and chloride concentrations occurred within the mid 1980s and the highest concentrations occurred in the early 1990s (a difference of about a factor of two);
3. there is an underlying annual structure with slightly higher concentrations during the early part of each year.

Figure 4 shows that the smoothed patterns follow each other for both sodium and chloride for two catchments. This feature is also shown clearly by statistical analysis of the unsmoothed data, which indicates a strong and highly significant linear feature for both sodium and chloride. Thus for sodium,

[Na (Upper Hore)] = 1.11 ± 0.06*[Na (Hafren)] – 22.0 ± 10.1 where $r^2 = 0.672$ and N = 750 when all the data points are included and [Na (Upper Hore)] = 1.08 ± 0.05*[Na (Hafren)] – 17.2 ± 9.0 where $r^2 = 0.710$ and N = 749 when one outlier point (as observed visually when the data are plotted against each other) is excluded. Correspondingly, for chloride: [Cl (Upper Hore)] = 1.16 ± 0.04*[Cl (Hafren)] – 25.4 ± 4.7 where $r^2 = 0.797$ and N = 746 when all the data points are included and [Cl (Upper Hore)] = 1.17 ± 0.03*[Cl (Hafren)] – 27.9 ± 6.9 where $r^2 = 0.863$ and N = 743 when three outlier points (as observed visually when the data are plotted against each other) are excluded.

In all these cases, the $\pm$ sign indicates plus or minus twice the standard error and the concentrations ([ ]) are represented in μ Eq l^{-1} units. Clearly the patterns observed are occurring across catchments and this implies that the processes operating are likely to be similar across the catchments.

Effects of clearfelling on sodium and chloride time series

A time series plot for the upper and lower Hore (Fig. 5) illustrates the effects of felling on sodium and chloride concentrations: the upper Hore acts as a control for the lower Hore which was felled between 1985 and 1989. The results show patterns similar to those described above, but with one noticeable difference: the lower Hore had higher concentrations of sodium and chloride before felling, reflecting its higher proportion of forest cover (Table 1). During the period of felling (1985 to 1989), sodium and chloride concentrations in the lower Hore declined, relative to upper Hore, reflecting decreased evaporation and decreased atmospheric scavenging of sea-salt aerosols.

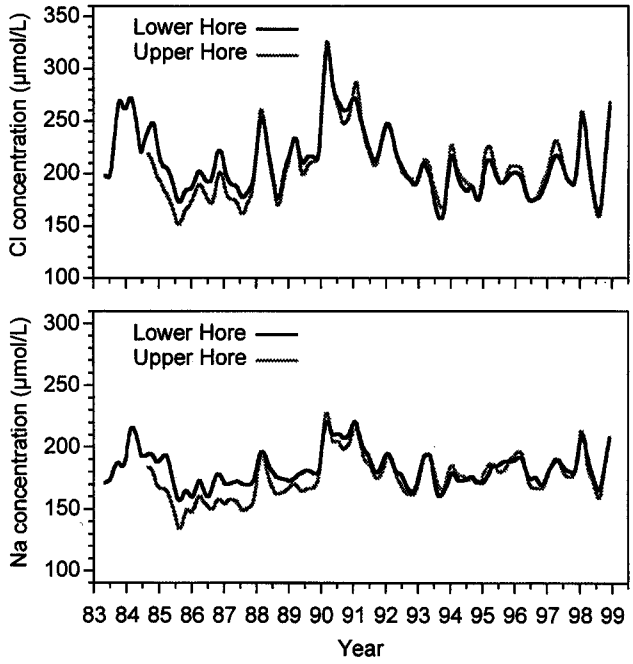

Fig. 5. *Ninety-day moving averages of chloride (top panel) and sodium (bottom panel) in streamflow at lower Hafren (black lines) and upper Hore (grey lines). The chloride concentration scale has been compressed by the sea-salt sodium/chloride ratio (0.86) to make the two scales comparable.*

Table 6. Linear regression analysis of sodium and chloride concentrations ([Na] = m*[Cl] + C) for rainfall, mist, stream waters and groundwaters.

	m	2*STD	C	2*STD	r^2	N
Atmospheric inputs						
Rain	0.783	0.015	−1	3	0.948	584
Mist	0.852	0.014	80	505	0.974	374
Main streams						
UHaf	0.369	0.040	93	6	0.448	431
LHaf	0.395	0.025	98	5	0.540	861
UHore	0.478	0.021	77	4	0.738	753
LHore	0.382	0.021	99	5	0.616	862
Intermediate size stream						
Tan	0.350	0.047	133	11	0.378	373
Small streams						
S2Hore	0.589	0.017	56	4	0.899	531
SE1f	0.462	0.065	151	17	0.639	117
SE3c	0.287	0.073	144	16	0.354	114
TanNc	0.431	0.050	108	12	0.762	96
TanSf	0.526	0.092	78	20	0.569	101
Boreholes						
HA4 b	0.549	0.161	155	49	0.260	135
SE1bf	0.244	0.128	197	33	0.141	91
SE3bc	0.238	0.070	211	22	0.340	92
TanNbc	0.474	0.159	105	43	0.222	126
TanSbf	0.175	0.136	212	39	0.053	122
US1	0.414	0.246	150	56	0.448	16
US2	0.418	0.152	145	13	0.699	15
US3	0.681	0.139	40	13	0.873	16
LS1	0.094	0.421	264	29	0.014	16
LS2	0.440	0.478	168	29	0.207	15
LS3	0.479	0.355	150	27	0.343	16
LS4	0.183	0.541	280	54	0.032	16
IS1	0.595	0.199	108	24	0.720	16
IS2	0.494	0.317	147	28	0.410	16
VB1	8.534	5.204	−1015	271	0.434	16

Following the period of felling, concentrations at the two sampling points became virtually indistinguishable (Fig. 5).

Sodium and chloride inter-relationships

The relationship between sodium and chloride concentrations in the Plynlimon waters separates into two groups, the atmospheric inputs and the streams/groundwaters.

ATMOSPHERIC INPUTS

Rainfall and mist show strong linear sodium-chloride relationships ($r^2 = 0.948$ and $r^2 = 0.974$, respectively). For rainfall the intercept is not statistically significant, whereas for mist the intercept is statistically significant but trivially small compared to the range of concentrations. For rainfall, the gradient is 0.783 (Table 6) which is slightly lower than that for sea-water (0.857): on a flow-weighted basis, the mean sodium to chloride ratio is nearer to that for sea-water at 0.81 (Table 4). For the mist, the gradient is 0.852 (Table

6) and the corresponding sodium to chloride ratio is 0.89. Thus, for both rainfall and mist, the sodium and chloride match the marine gradient and ratio reasonably well. This is to be expected given the maritime influence of sea salts from atmospheric sources: the mist has a slightly higher gradient and ratio probably due to a small non-sea-salt component.

STREAMS AND GROUNDWATERS

For the streams and groundwaters, the flow-weighted average sodium to chloride ratio is similar to, or slightly higher than, the ratio for sea-water and rainfall (for the groundwaters, no flows were available for the weighting and the straight averages were therefore used). This again illustrates the significance of the marine input. However, the groundwater at VB1 had an exceptionally high Na/Cl ratio, as well as much higher alkalinities and base cation concentrations, reflecting a much greater supply of sodium and other base cations from weathering (Neal *et al.*, 1997c). This exceptional site is not referred to in the remainder of the paper.

Linear relationships are observed between sodium and chloride concentrations for the streams and groundwaters, but their gradients are significantly lower than those of either sea water or the atmospheric inputs, and there is a statistically significant intercept (Table 6, Fig. 6). This means that some process other than simple dilution and evapoconcentration regulates either sodium or chloride. As mentioned in the introduction, ion exchange reactions should buffer the concentration of sodium relative to chloride, by releasing sodium from cation exchange sites when concentrations are low, and absorbing sodium onto ion exchange sites when concentrations are high. Here, chloride concentrations provide an indication of the total sodium added to the catchments, and thus the degree to which sodium has been either adsorbed or released. For example, the Na/Cl ratio in the upper Hore streamflow (Fig. 6b) is generally higher than the sea-salt ratio when chloride concentrations are low indicating release of additional sodium from ion exchange sites. Correspondingly, the ratio in upper Hore stream water is lower than the sea-salt ratio when chloride concentrations are high indicating adsorption of sodium onto cation exchange sites. Whereas the Na/Cl ratio in rainfall does not change systematically with chloride concentration ($r^2 < 0.01$, $p > 0.2$), the Na/Cl ratio in the upper Hore streamflow decreases systematically with increasing chloride ($r^2 = 0.48$, $p < 0.0001$), consistent with the pattern one would expect from ion exchange processes.

There are two aspects to note at the more detailed level. Firstly, the sodium to chloride gradients in the streams and the groundwaters vary. This result is explained partly by data scatter where the standard error in the estimate can be high. However, for some sites there are statistically significant variations in gradients. This feature implies a

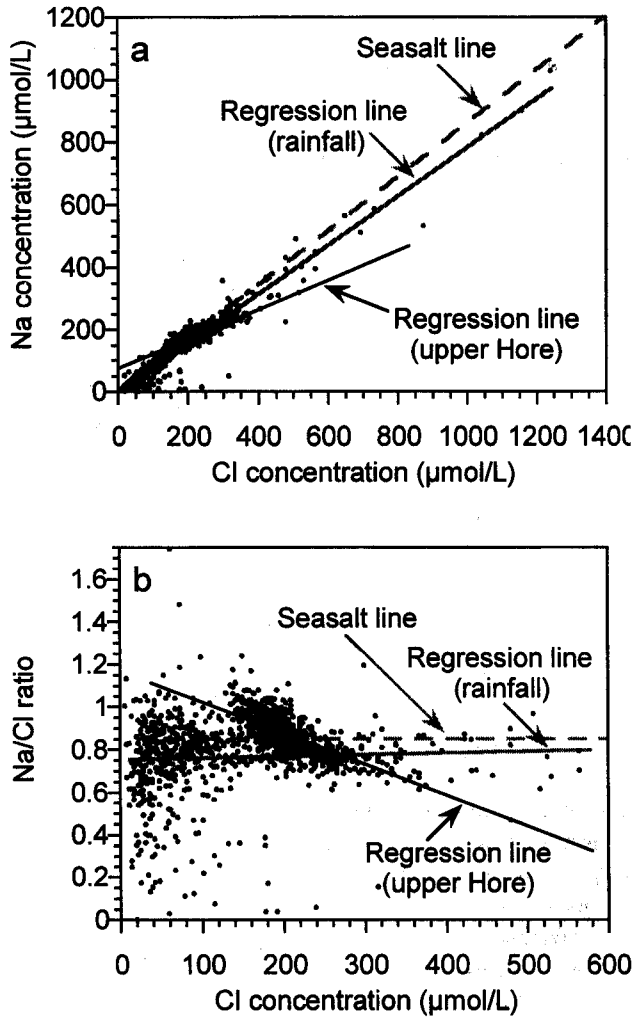

Fig. 6. *Relationship between sodium and chloride in rainfall and upper Hore streamflow. Rainfall samples fall close to the relationship expected for sea-salt, whereas streamflow samples deviate systematically from it, with a significantly lower slope (panel a). The Na/Cl ratio in streamflow overlaps with the sea-salt ratio (Na/Cl = 0.86) but decreases systematically with increasing chloride concentration, reflecting buffering by ion exchange processes (panel b).*

variation in the extent of the cation exchange reactions within the catchments. Secondly, there may be anion exchange processes involved for chloride and the sodium to chloride ratio reflects the net balance between cation and anion exchange for these two ions. The results imply that the cation exchange reaction for sodium is much greater than the anion exchange reaction for chloride (if anion exchange were dominant then the sodium to chloride gradient in the streams would be greater than that for rainfall). This is to be expected as the soil exchangers within the catchment are cation exchange dominated and the anion uptake of chloride is relatively weak (indeed, anions may even be negatively adsorbed - i.e. excluded from near the negatively charged exchange surfaces).

Autocorrelation and cross-correlation in sodium and chloride time series

The autocorrelations and cross-correlations of the rainfall and streamflow concentrations further illustrate the contrast between sodium and chloride dynamics in the Plynlimon catchments. The autocorrelation function measures the correlation between points on a time series, as a function of the lag interval between them. Thus, it quantifies how tightly a concentration time series is correlated with itself through time. Because the sampling schedule was not precisely periodic (particularly for rainfall, because in some sampling periods only trace amounts of rain were collected and therefore concentrations could not be measured), it is necessary to use a geostatistical approximation to the Pearson product-moment autocorrelation in rainfall or streamflow (Kirchner and Weil, 2000a):

$$r(\tau) = \frac{\langle (X_i - \langle X_i \rangle)(X_j - \langle X_j \rangle) \rangle}{\sqrt{\langle (X_i - \langle X_i \rangle)^2 \rangle} \sqrt{\langle (X_j - \langle X_j \rangle)^2 \rangle}}$$

$$\forall i,j : \tau - \frac{\Delta\tau}{2} < t_j - t_i < \tau + \frac{\Delta\tau}{2} \qquad (1)$$

where $r(\tau)$ is the autocorrelation at a lag of τ, and X_i and X_j are concentrations at all pairs of points whose separations in time, $t_j - t_i$, fall within a bin of width $\Delta\tau$ centred around τ. Here, because the sampling frequency is roughly weekly, autocorrelations are calculated every $\Delta\tau = 7$ days. The resulting autocorrelation functions show that both sodium and chloride concentrations in rainfall rapidly become decorrelated with one another beyond lags of one or two weeks (dashed lines, Fig. 7). The seasonal fluctuations in rainfall concentrations give rise to positive autocorrelations at lags of whole years, and negative autocorrelations at the intervening half-year lags. In contrast to rainfall, streamflow concentrations of both sodium and chloride remain strongly autocorrelated out to lags of roughly 1.5 years (solid lines, Fig. 7). This demonstrates a strong "memory effect" resulting from the storage and mixing of waters in the catchment.

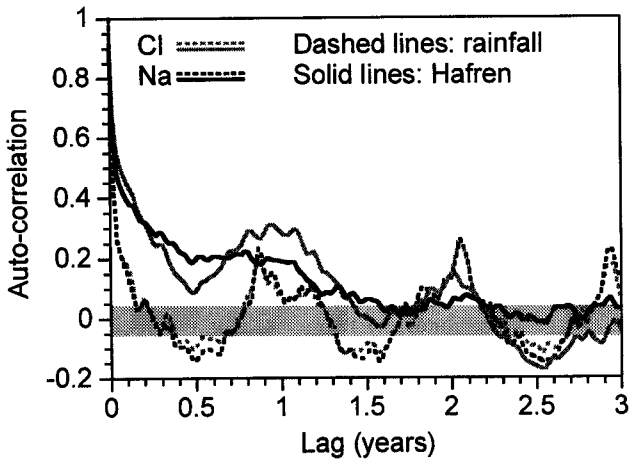

Fig. 7. *Autocorrelation in sodium and chloride concentrations (black and grey lines, respectively) in rainfall (dashed lines) and lower Hafren streamflow (solid lines). Shaded band delimits upper and lower 5% confidence limits for autocorrelations in randomly re-shuffled (and therefore uncorrelated) time series.*

The autocorrelation function for streamflow chloride exhibits marked seasonality, with relatively high values at whole-year lags and relatively low values in the intervening half-years, whereas the autocorrelation function for streamflow sodium reflects much less seasonality (Fig. 7). This implies that ion exchange buffering is sufficient to attenuate strongly the seasonality that would otherwise occur in streamflow sodium concentrations. The chloride autocorrelations imply that hydrological storage and mixing is sufficient to generate significant chemical "memory" in the catchment, but not to overcome the seasonality imparted by deposition. The sodium autocorrelations imply that ion exchange buffering has the added effect of largely suppressing the seasonal effects of the sodium input signal.

This hypothesis can be further explored using the cross-correlation between concentrations in rainfall and runoff. Cross-correlation functions measure how closely two time series resemble each other, when one is shifted forward or backward by a specified interval. Thus, they provide a direct measure of the lag between chemical inputs in rainfall and chemical outputs in streamflow. A geostatistical approximation to the cross-correlation function is (Kirchner and Weil, 2000):

$$r(\tau) = \frac{\langle (I_i - \langle I_i \rangle)(O_j - \langle O_j \rangle) \rangle}{\sqrt{\langle (I_i - \langle I_i \rangle)^2 \rangle} \sqrt{\langle (O_j - \langle O_j \rangle)^2 \rangle}}$$

$$\forall i,j : \tau - \frac{\Delta\tau}{2} < t_j - t_i < \tau + \frac{\Delta\tau}{2} \qquad (2)$$

where I and O are concentrations in inputs (rainfall) and outputs (streamflow), respectively, at all pairs of points whose separations in time, $t_j - t_i$, fall within a bin of width $\Delta\tau$ centred around τ. The cross-correlation between chloride in rainfall and streamflow exhibits pronounced seasonality, reflecting the seasonality of the rainfall concentrations, and a relatively strong cross-correlation out to lags of roughly three months (Fig. 8). The cross-correlation between sodium concentrations in rainfall and streamflow is substantially weaker, indicating that factors other than rainfall concentrations have a bigger effect on sodium than on chloride, and thus do more to obscure the correlation with rainfall inputs. The cross-correlation function for sodium exhibits substantially less seasonality than the cross-correlation for chloride, again suggesting that ion exchange buffers the seasonal fluctuations that would otherwise occur in sodium.

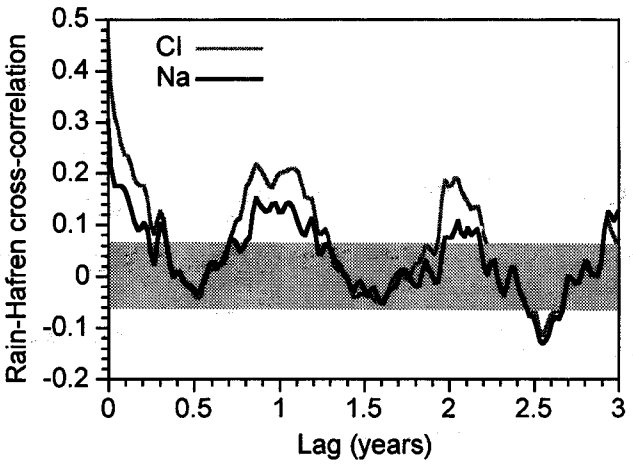

Fig. 8. *Cross-correlation between concentrations in rainfall and subsequent concentrations in lower Hafren streamflow. Chloride concentrations exhibit stronger cross-correlation (grey lines) than sodium concentrations (black lines). Shaded band delimits upper and lower 5% confidence limits for cross-correlations between randomly re-shuffled time series (that is, time series lacking any intrinsic cross-correlation).*

Discussion and conclusions

As explained in the introduction, this analysis is focused on three issues, which are addressed individually below.

1. To what extent are atmospheric inputs of sodium and chloride damped within catchments?

As with many previous studies, the Plynlimon data show that both sodium and chloride inputs are damped within the streams. However, the present data adds to knowledge in three important ways. Firstly, most of the earlier long term work for Plynlimon related to water storage has been confined to chloride: the present study shows similar broad behaviour for sodium. Secondly, the analysis of weekly data, in conjunction with Kirchner *et al.*'s analysis of daily chloride measurements in Hafren and Tanllwyth (Kirchner *et al.*, 2000) demonstrates strong damping of rainfall inputs on all timescales, from days to several years. The damping for the daily stream chemistry time series is higher than for the much longer weekly record (Table 2). This implies that the longer term changes in atmospheric input have a larger proportionate influence on the chloride variations consistent with the spectral analysis of Kirchner *et al.* (2000). Thirdly, many previous studies have paid little regard to the importance of groundwater transport of chemicals in these supposedly impermeable catchments (Neal *et al.*, 1997a,b,c). The earlier work at Plynlimon shows clearly that groundwater is an important and volumetrically significant water store. However, the present study indicates a high degree of sodium and chloride damping even in such a highly fracture-flow dominated system.

2. How uniform is the damping across the catchments?

The present study shows that rainfall inputs affect the streamflow chemistry of the individual catchments in similar ways, and the chemical time series of different catchments are highly correlated. This finding is remarkable given the heterogeneous nature of the catchments and the complexity of the (fractal) chemical time series signal in the streams (Kirchner *et al.*, 2000).

3. Do cation exchange processes regulate sodium mobility within catchments as seen within the stream and the groundwater?

The results show clearly that the sodium to chloride gradients in the streams and groundwaters differ from the gradients in the atmospheric input, despite the lack of internal catchment sources for either sodium or chloride. The pattern of behaviour for the streams and groundwaters is consistent with cation exchange processes regulating sodium concentrations. Thus as outlined in the introduction:

- as salt (NaCl) concentration increases above the norm, more sodium is taken onto the soil cation exchange sites thus lowering the sodium to chloride ratio.
- as salt (NaCl) concentration decreases below the norm, more sodium is displaced from the soil cation exchange sites thus increasing the sodium to chloride ratio.

Such changes are of course balanced by changes in the other major cations (Ca, Mg and K) and acidification components (hydrogen ions and inorganic aluminium). However, the changes in the other cations are largely masked owing to their scatter as influenced by hydrological variability (Neal *et al.*, 1998a,b). The effect of this cation exchange control is to dampen the rainfall sodium signal even more strongly than the purely hydrological damping of the rainfall chloride signal.

Closing comments

The present study adds to understanding of the water quality functioning of acidic and acid sensitive catchments dominated by fracture flow catchment systems and complex hydrology. The work demonstrates the value of examining the attenuation of a range of chemicals with contrasting hydrochemical behaviour: a start has been made to clarify the key chemical and hydrological controls. If sodium and other reactive species are buffered by exchange reactions with catchment soils, their travel times through the catchment should differ systematically from the travel time of water and its non-reactive tracers (such as chloride). The work of Kirchner *et al.* (2000) illustrates how catchment travel times can be estimated from spectral analysis of chemical time series in rainfall and streamflow. The logical next step is to use spectral methods to estimate travel time distributions for sodium and other reactive species, to better

assess how exchange buffering affects ion mobility at catchment scale. This is particularly important with regards to elements of contrasting hydrogeochemical behaviour (Neal, 2000). Understanding the functioning of hydrologically and hydrochemically complex catchment systems is a critical challenge for the environmental modelling community (Neal, 1997b; Kirchner *et al.*, 2000).

References

Christophersen, N. and Neal, C., 1990. Linking hydrological, geochemical, and soil chemical processes on the catchment scale: an interplay between modelling and field work. *Wat. Resour. Res.*, **26**, 3077–3086.

Christophersen, N., Seip, H.M. and Wright, R.F., 1982. A model for stream water chemistry at Birkenes, Norway. *Wat. Resour. Res.*, **18**, 977–996.

Christophersen, N., Rustad, S. and Seip, H.M., 1984. Modelling streamwater chemistry with snowmelt. *Philos. Trans. Royal, Soc.*, London, B, **305**, 427–439.

Christophersen, N., Neal, C. and Hooper, R.P., 1993. Modelling the hydrochemistry of catchments: a challenge for the scientific method. *J. Hydrol.*, **152**, 1–12.

Cosby, B.J., Wright, R.F., Hornberger, G.M. and Galloway, J.N., 1985a. Modelling the effects of acidic deposition: assessment of a lumped-parameter model of soil water and stream water chemistry. *Wat. Resour. Res.*, **21**, 51–63.

Cosby, B.J., Wright, R.F., Hornberger, G.M. and Galloway, J.N., 1985b. Modelling the effects of acid deposition: estimation of long-term water quality responses in a small forested catchment. *Wat. Resour. Res.*, **21**, 1591–1601.

Cryer, R., 1986. Atmospheric solute inputs. In: *Solute Processes* (ed: S.T. Trudgill), John Wiley, Chichester, UK, 15–84.

Drever, J.I., 1997. *The geochemistry of natural waters.* Prentice Hall (Upper Saddle River, NJ), 1–433.

Garrels, R.M., and Christ, C.L., 1965. *Solutions, minerals and equilibria.* Harper and Row (New York), 450pp.

Hooper, R.P., Stone, A., Christophersen, N., de Grosbois, E. and Seip, H.M., 1988. Assessing the Birkenes model of stream acidification using a multisignal calibration methodology, *Wat. Resour. Rese.*, **24**, 1308–1316.

Hudson, J.A., Crane, S.B. and Blackie, J.R., 1997. The Plynlimon water balance 1969–1995: The impact of forest and moorland vegetation on evaporation and streamflow in upland catchments. *Hydrol. Earth System Sci.*, **1**, 409–428.

Kämäri, J., Brakke, D.F., Jenkins, A., Norton, S.A. and Wright, R.F., 1989 (eds). *Regional acidification Models.* Springer Verlag (Berlin), 306pp.

Kirchner, J.W., 1992. Heterogeneous geochemistry of catchment acidification. *Geochimica et Cosmochimica Acta*, **56**, 2311–2327.

Kirchner, J.W., Hooper, R.P., Kendall, C., Neal, C. and Leavesley, G., 1996. Testing and validating environmental models, *Sci. Total Envir.*, **183**, 33–47.

Kirchner, J.W., Feng, X.H. and Neal, C., 2000. Fractal stream chemistry and its implications for contaminant transport in catchments. *Nature*, **403**, 524–527.

Kirchner, J.W. and Weil, A., 2000a. Correlations in fossil extinctions and originations through geologic time, *Proc. Roy. Soc. London B*, **267**, *1301–1319.*

Kirchner, J.W. and Weil, A., 2000b. Delayed biological recovery from extinctions throughout the fossil record, *Nature*, **404**, 177–180.

Mason, B.J., 1990. *The surface water acidification programme. A compendium of papers* edited by B.J. Mason. Cambridge University Press, 522pp.

Neal, C. and Christophersen, N., 1989. Inorganic aluminium-hydrogen ion relationships for acidified streams: the role of water mixing processes. *Sci. Total Environ.*, **80**, 195–203.

Neal, C., Christophersen, N., Neale, R., Smith, C.J., Whitehead, P.G. and Reynolds, B., 1988. Chloride in precipitation and streamwater for the upland catchment of the River Severn, mid-Wales; some consequences for hydrochemical models. *Hydrol. Processes*, **2**, 155–165.

Neal, C., Smith, C.J., Walls, J., Billingham, P., Hill, S. and Neal, M., 1990a. Hydrochemical variations in Hafren Forest stream waters, mid-Wales. *J. Hydrol.*, **116**, 185–200.

Neal, C., Robson, A.J. and Smith, C.J., 1990b. Acid neutralization capacity variations for the Hafren Forest stream, mid-Wales: inferences for hydrological processes. *J. Hydrol.*, **121**, 85–101.

Neal, C., Smith, C.J. and Hill, S., 1992. *Forestry impact on upland water quality.* Institute of Hydrology No. 119. Institute of Hydrology, Wallingford, UK. 50pp.

Neal, C., 1997a (ed). Water quality of the Plynlimon catchments (UK). *Hydrol. Earth System Sci.*, **1**, 381–766.

Neal, C., 1997b. A view of water quality from the Plynlimon watershed. *Hydrol. Earth System Sci.*, **1**, 743–754.

Neal, C., 2000. Catchment science in a heterogeneous world: reflections on the water quality functioning of the Plynlimon catchments, Plynlimon, mid-Wales. In: *Water in the Celtic Wold: managing resources for the 21st century* (eds. J.A.A. Jones, K. Gilman, A. Jigorel and J. Griffin). BHS Occasional Paper, **11**, 189–196.

Neal, C., Robson, A.J. and Christophersen, N., 1997a. Towards coupling hydrological, soil and weathering processes within a modelling perspective. In: *Geochemical processes, weathering and groundwater recharge in catchments* (eds O.M. Saether and P. de Caritat). Balkema, Rotterdam, 329–380.

Neal, C., Hill, T., Hill, S. and Reynolds, B., 1997b. Acid neutralization capacity measurements in surface and groundwaters in the upper River Severn, Plynlimon, mid-Wales: from hydrograph splitting to water flow pathways. *Hydrol. Earth System Sci.*, **1**, 687–696.

Neal, C., Robson, A.J., Shand, P., Edmunds, W.M., Dixon, A.J., Buckley, D.K., Hill, S., Harrow, M., Neal, M. and Reynolds, B., 1997c. Stream water quality in acid sensitive upland areas, an example of potential water quality remediation based on groundwater manipulation. *Hydrol. Earth System Sci.*, **1**, 3–18.

Neal, C., Hill, T., Alexander, S., Reynolds, B., Hill, S., Dixon, A.J., Harrow, M., Neal, M. and Smith, C.J., 1997d. Stream water quality in acid sensitive upland areas, an example of potential water quality remediation based on groundwater manipulation. *Hydrol. Earth System Sci.*, **1**, 185–196.

Neal, C., Wilkinson, J., Neal, M., Harrow, M., Wickham, H., Hill, L. and Morfitt, C., 1997e. The hydrochemistry of the River Severn, Plynlimon, mid-Wales. *Hydrol. Earth System Sci.*, **1**, 583–618.

Neal, C., Reynolds, B., Adamson, J.K., Stevens, P.A., Neal, M., Harrow, M. and Hill, S., 1998a. Analysis of the impacts of major anion variations on surface water acidity particularly with regard to conifer harvesting: case studies from Wales and Northern England. *Hydrol. Earth System Sci.*, **2**, 303–322.

Neal, C., Reynolds, B., Wilkinson, J., Hill, T., Neal, M., Hill, S. and Harrow, M., 1998b. The impacts of conifer harvesting on runoff water quality: a regional survey for Wales. *Hydrol. Earth System Sci.*, **2**, 323–344.

Robson, A.J., 1993. *The use of continuous measurement in understanding and modelling the hydrochemistry of the uplands.* PhD dissertation, University of Lancaster, Lancaster, Lancashire, UK, 278pp.

Wilkinson, J., Reynolds, B., Neal, C., Hill, S., Neal, M. and Harrow, M., 1997. Major, minor and trace element composition of cloudwater and rainwater at Plynlimon, mid-Wales. *Hydrol. Earth System Sci.*, **1**, 557–570.